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NATIONAL LABORATORY

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Fundamental Challenges and Opportunities— Low Temperature Activation

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Carbon Recycling for fuels and chemicals for minimizing the CO₂ footprint of US industry.

More than 80% of all conversions in refinery are catalyzed.

Improve/re-invent
chemical and refining
processes

Offer solutions for zero
carbon footprint

Minimize land and water
use through C recycling

A large fraction of the
energy from fossil fuels
can be substituted by
renewable sources.

**Heat integration is key
to process economy**

Catalysis is the key to realizing this change!

Heat integration is challenging

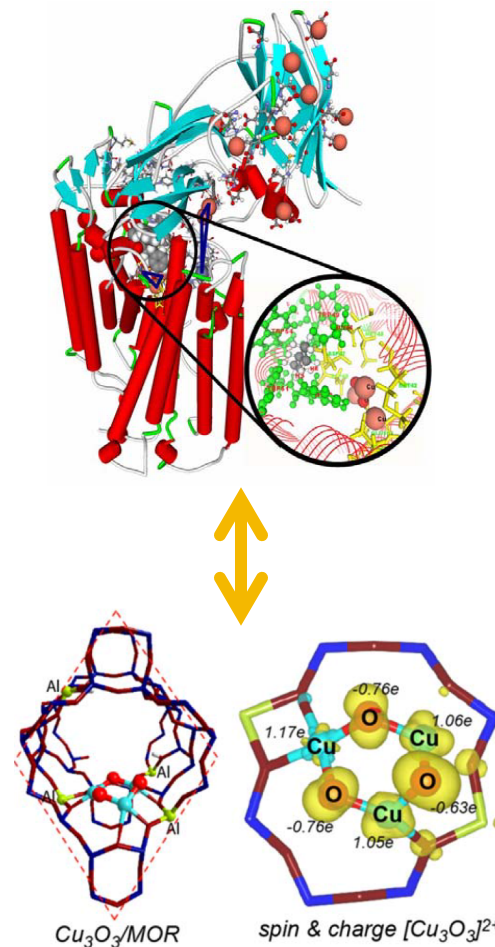
The transformational science need is to increase the rates of lower T processes

- ▶ Learn from nature, how to synthesize molecules at an unprecedented combination of rate and selectivity
 - What are the design rules that allow the rates and control of enzymes?

Understand, abstract, and minimize the complexity of three-dimensional sites as found in enzymes

- What are the synthesis rules for inorganic catalysts?

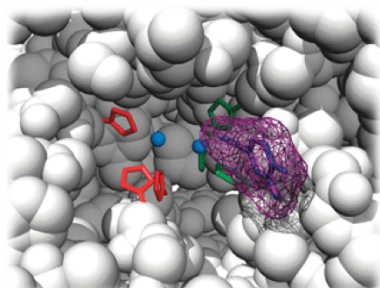
Devise strategies to synthesize materials with high density of catalytically active sites having a tailored chemically functionalized steric environment.



Need to increase reaction rates at low temperatures by one million fold

Elevating reaction rates

Biology

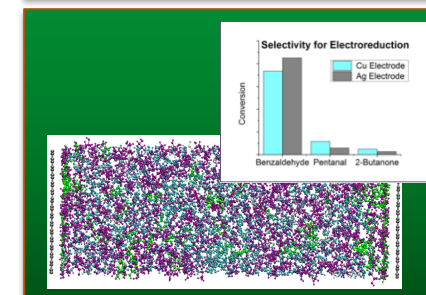
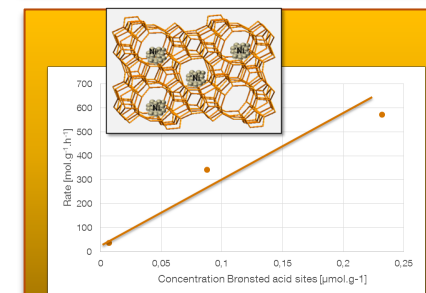
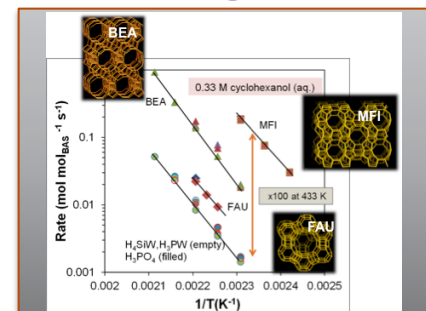


Constrained space
10 – 1000 x rate

Multifunctional active sites
10 – 1000 x rate

Channels for proton &
molecule delivery
10 – 1000 x rate / selectivity

Inorganic



A combination of these features to obtain the required rate enhancement relative to currently available.

Bringing all the capabilities together synergistically.

Thermodynamics of adsorption

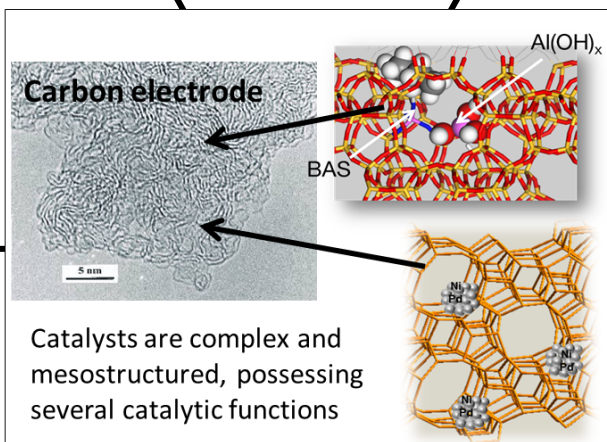
Calorimetric measurements and determination of enrichments and preferential adsorption

Assessment of catalytic properties

Kinetic measurements establishing rates, activation energies and entropies

State of catalyst – in situ monitoring

IR, SFG and NMR spectroscopy, XAS, STEM, SEM



Following elementary reaction steps

¹³C MAS NMR and IR spectroscopy, isotope labelling

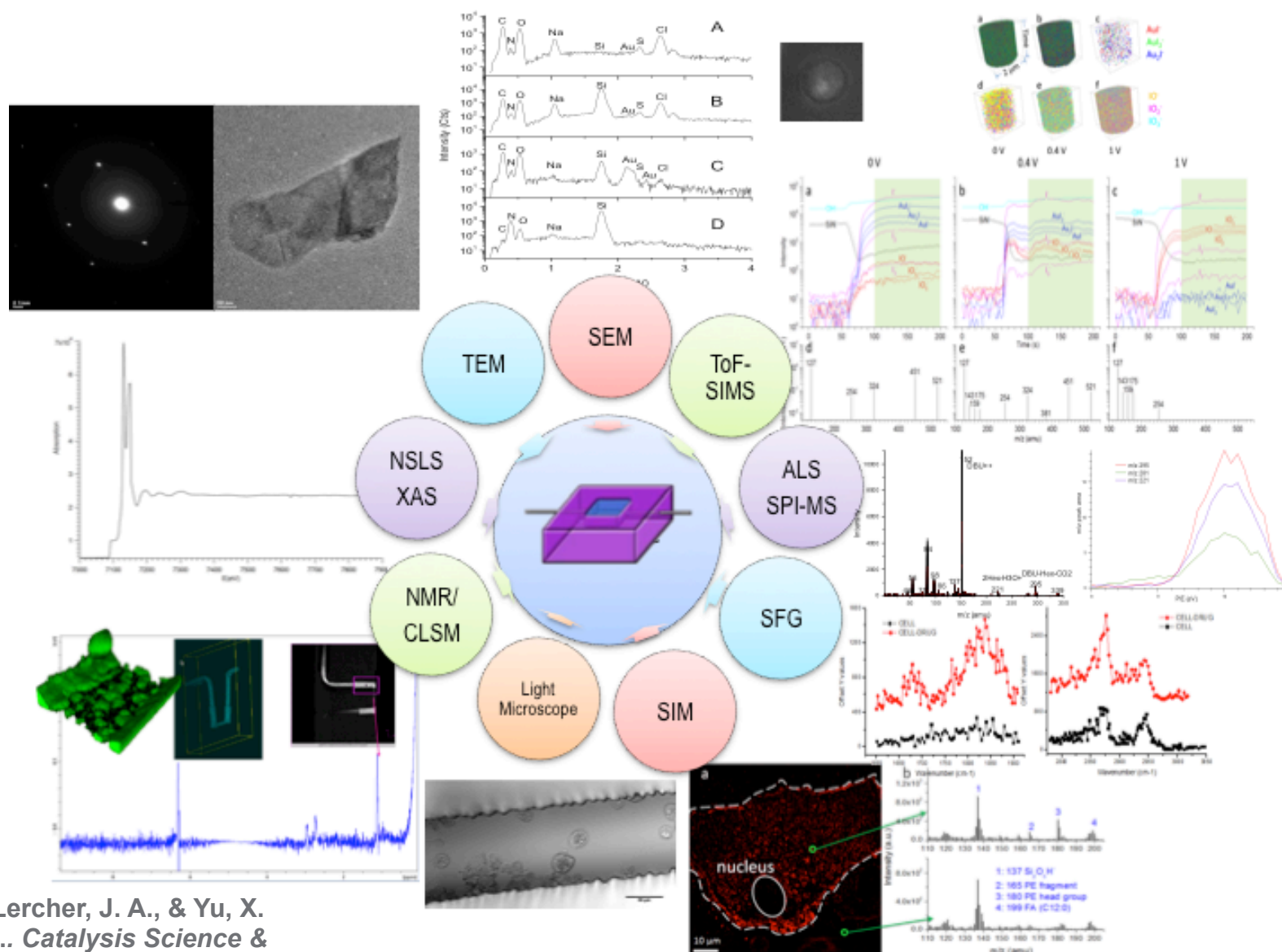
Theory

Wide variety of theoretical methods accounting explicitly for solvent molecules

Synthetic approaches

Embed metal particles (Pt, Pd, Ni, Co, Fe, Cu) in three-dimensional functionalized environment

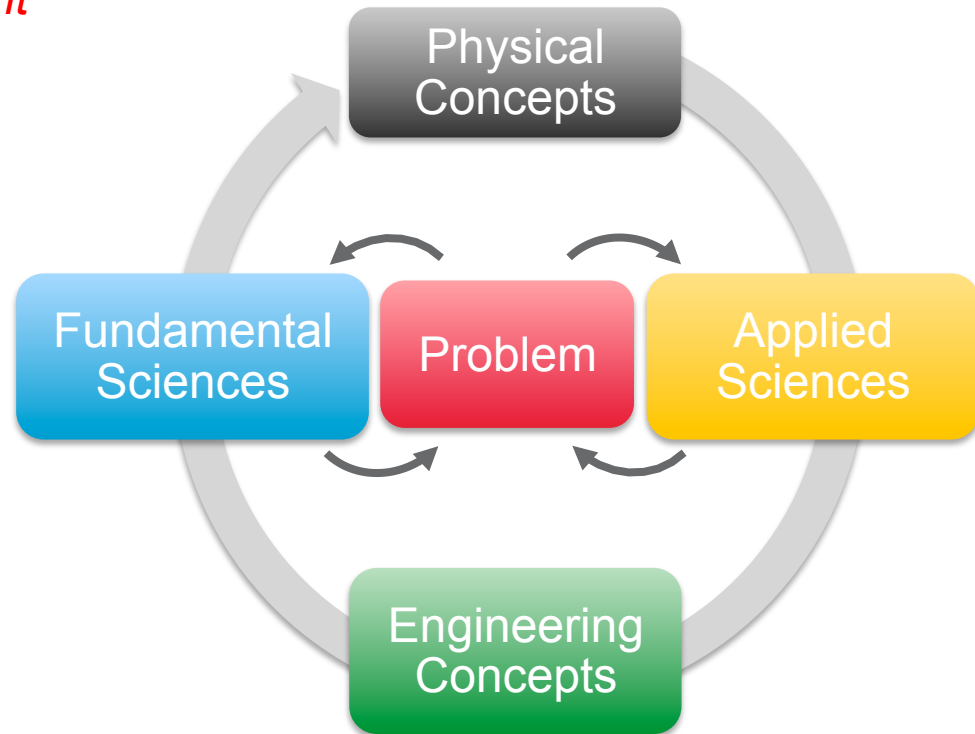
Microfluidic reactors allow for multimodal imaging and spectroscopy for solid liquid interfaces



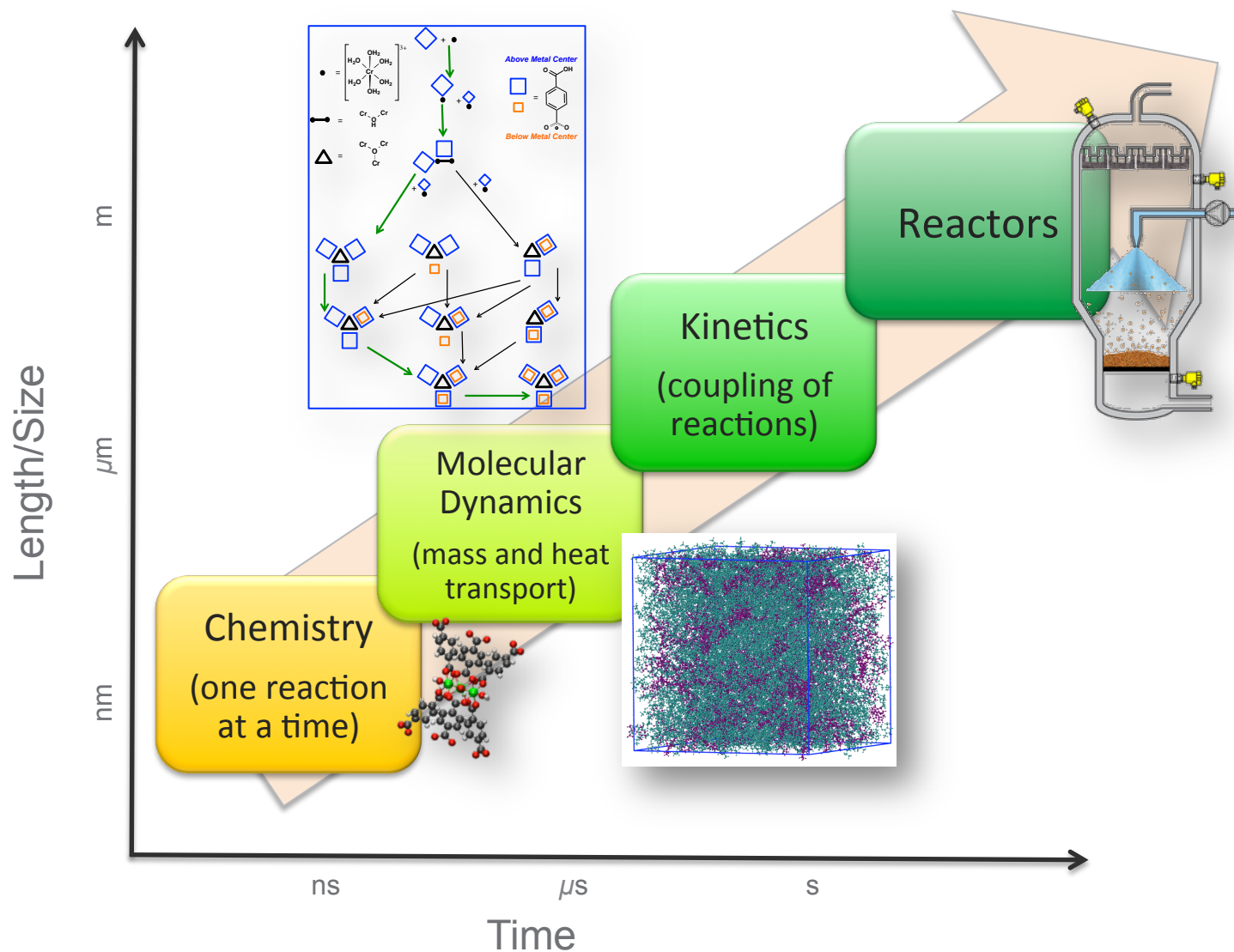
Shi, H., Lercher, J. A., & Yu, X. Y. (2015).. *Catalysis Science & Technology*, 5, 3035-3060.

Our fundamental science fully integrated with concurrent technology studies.

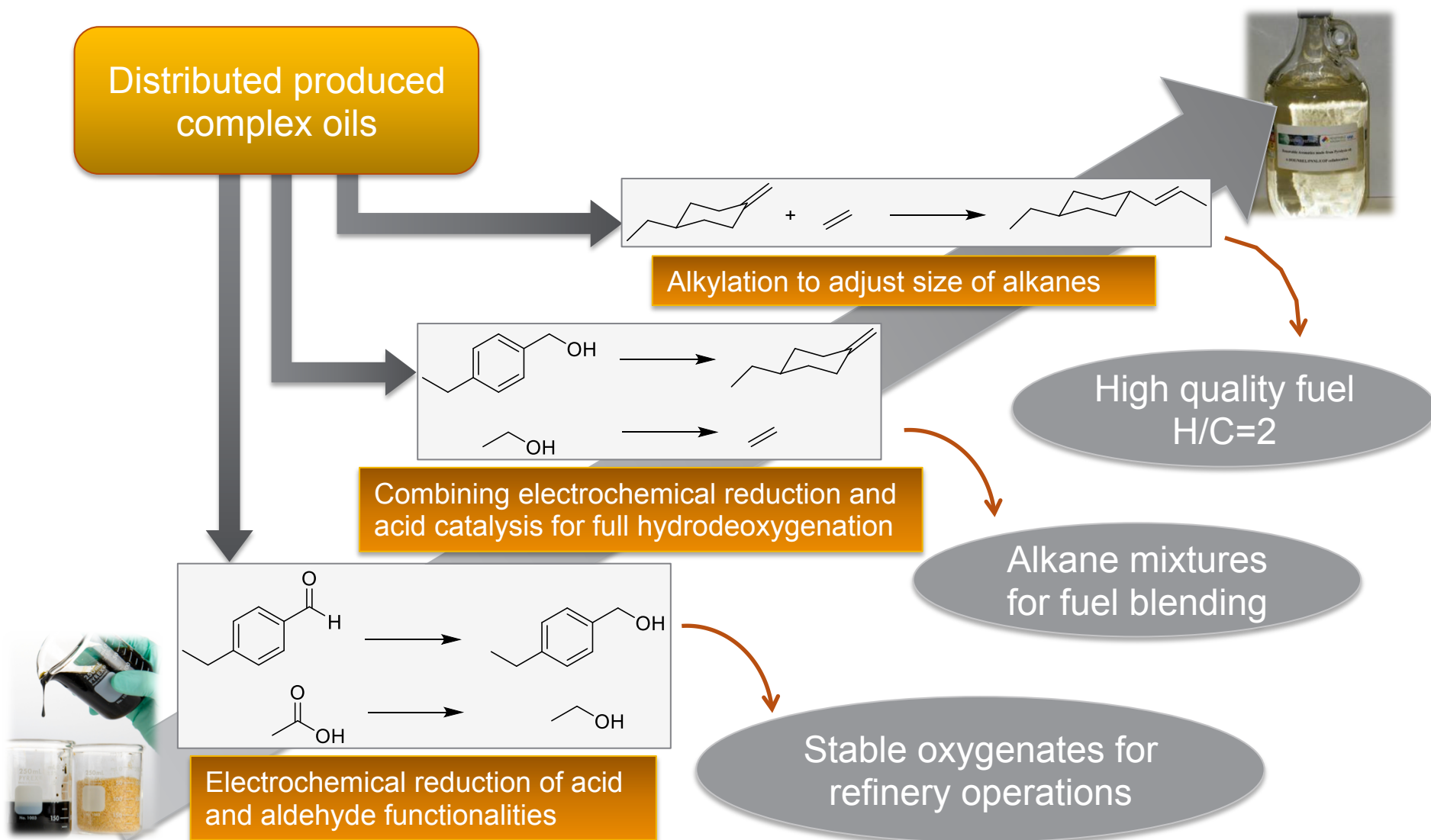
- ▶ Integrate efforts *directly with concurrent experimental efforts*
- ▶ Use science studies as a tool for *hypothesis generation* to guide research efforts and accelerate development
- ▶ Need a variety of methods that span multiple length/time scales:
 - To capture the relevant physics/chemistry
 - To make substantive contributions to our understanding of complex processes.
 - Adapt methodology to each problem instead of fitting the problem to the favorite method.



A hierarchy of different scale approaches is needed to address problems



Phased approach to carbon-neutral fuels



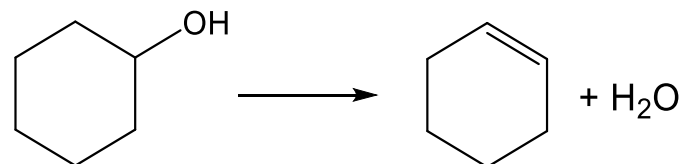
How to increase rates through steric constraints

Case 1

Cyclohexanol dehydration - a critical step in the bifunctional hydrodeoxygenation



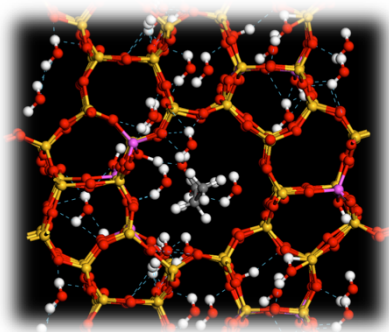
$\text{H}_3\text{PO}_4/\text{H}_2\text{O}$



Rate per mol $\text{H}_3\text{O}^+ = 15 \text{ h}^{-1}$

$E_a = 120 \text{ kJ/mol}$

200°C



zeolite/ H_2O

Rate per mol $\text{H}_3\text{O}^+ = 1600 \text{ h}^{-1}$

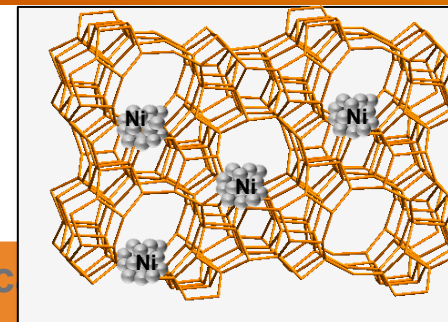
$E_a = 115 \text{ kJ/mol}$

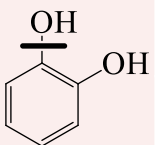
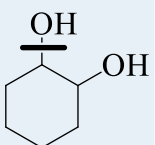
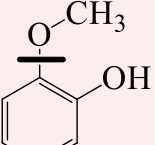
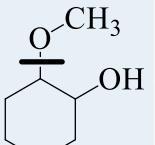
- Higher transition entropy in zeolite appears to drastically accelerate conversion

We are combining acid base functions and hydrogenation functions into confined spaces

Case 2

Hydrogenolysis of ethers – the critical step in the decomposition of lignin

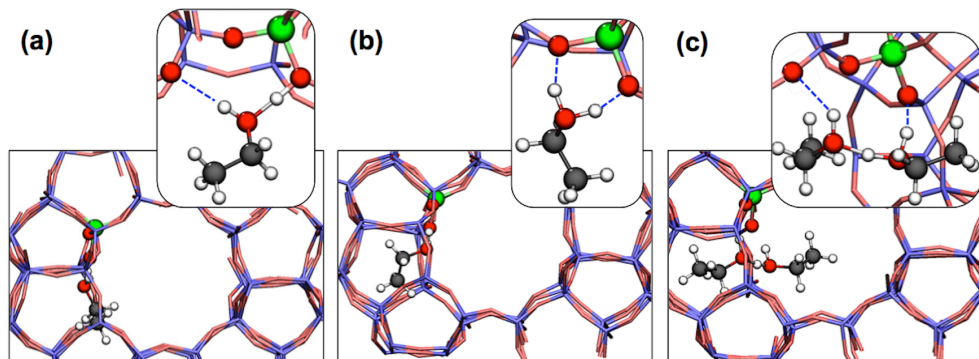


Entry	C-O cleavage pathway	Active sites	TOF with different catalysts (h ⁻¹)		
			Ni/HZSM-5	HZSM-5	Ni/SiO ₂
	Hydrogenation	Ni ^a	334	-	3.4
	Hydrogenolysis	Ni ^a	83	-	2.2
	Hydrogenolysis	Ni ^b	93	-	11
	Dehydration	[H ₃ O] ^{+b} _{MFI}	50	19	-
	Hydrogenation	Ni ^a	43	-	0.2
	Hydrogenolysis	Ni ^a	86	-	1.0
	Hydrogenolysis	Ni ^b	1.5	-	0.5
	Demethoxylation	[H ₃ O] ^{+b} _{MFI}	3.9	4.7	-

^a Temperature: 200 °C, ^b Temperature: 250 °C

Funding Source DOE-BES

Anharmonicity plays a critical role on thermodynamics in confined pores



► Scientific Challenge

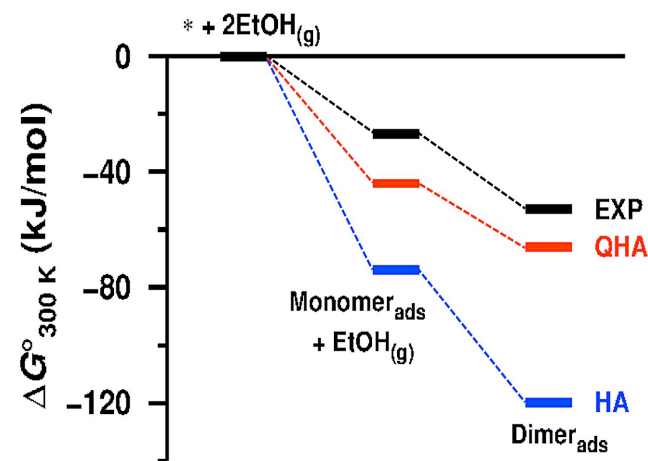
- Understanding and representing the entropic effects of confinement.

► Scientific Results

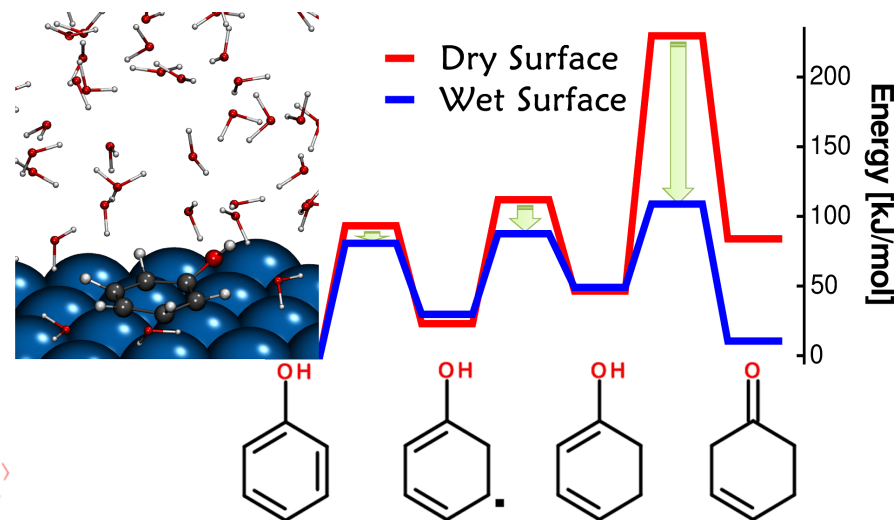
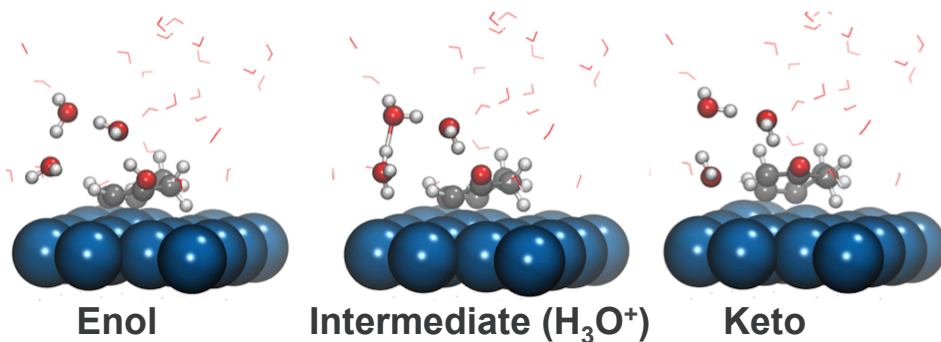
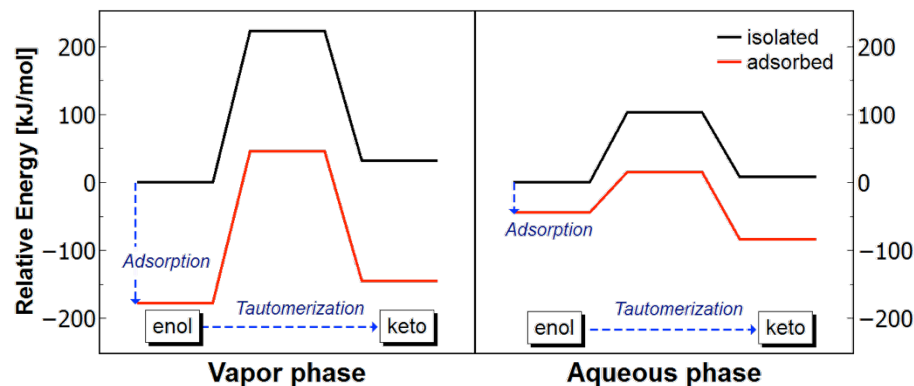
- Quantitative evaluation of Ethanol adsorption free-energetics in ZMS-5 and pertinent mechanistic details.
- Inclusion of anharmonicity is critical and can be evaluated quantitatively from AIMD, using a quasi-harmonic approximation.

► Why It Matters

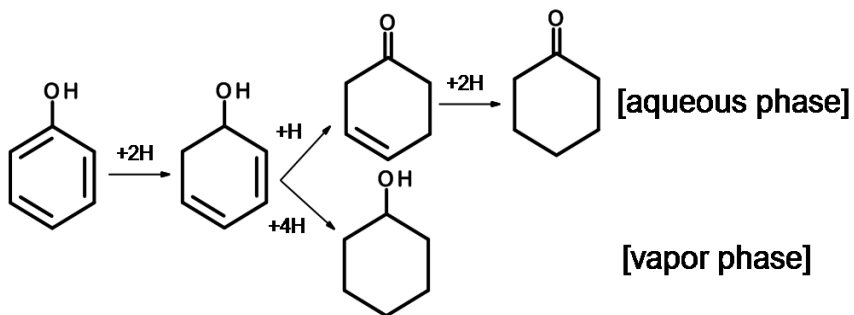
- Rate enhancement from confinement is highly dependent upon anharmonicity.



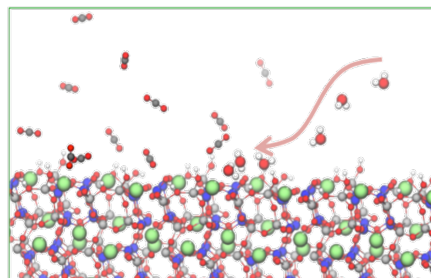
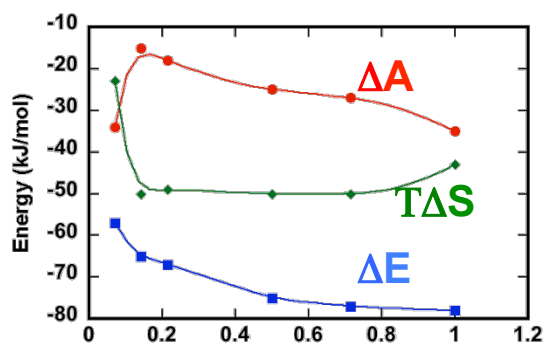
Building on our expertise in condensed phase chemical physics we are investigating catalysis in liquids



- ▶ We need to understand how hydrogenation mechanics differ between solid/vapor and solid/liquid interfaces
- ▶ Combining kinetics, spectroscopy and simulations allows us to understand catalyst structure and local reaction environment and its influence on reactivity in the liquid phase



Liquid environments can lead to unique speciation and structural transformations that can impact catalysis



Scientific Achievement

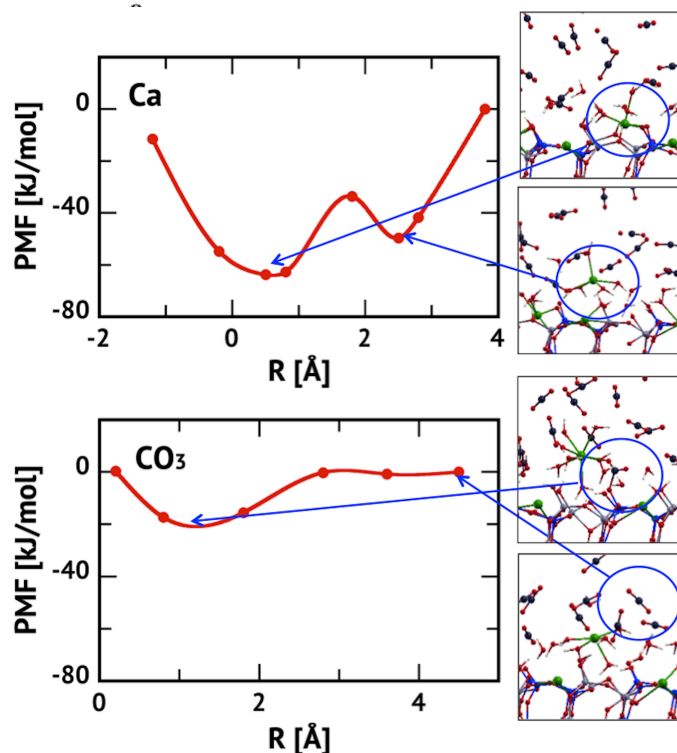
- AIMD simulations of water film growth in scCO₂ shows that even very low water concentrations can lead to a liquid-water boundary layer on anorthite(001)
- Reactivity to form cation vacancies is facilitated by water.

Significance

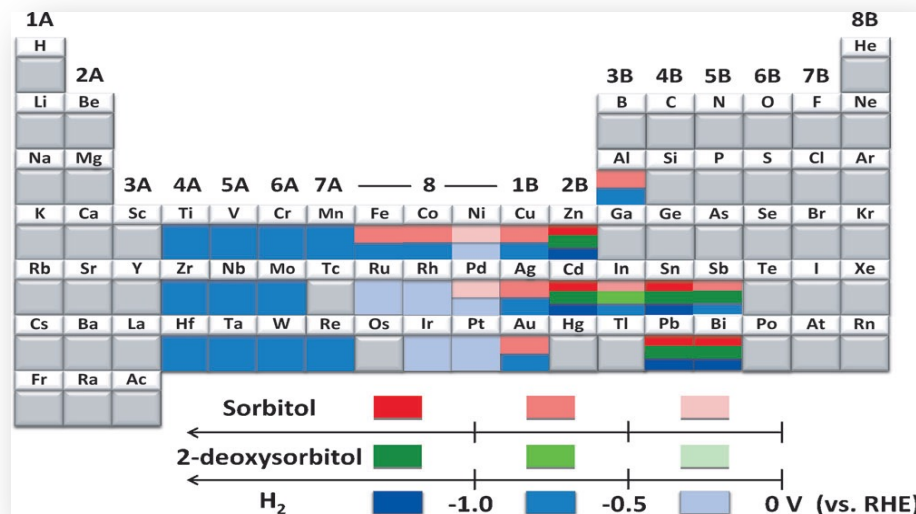
- Catalysis for reaction that produce water (ex CO₂ hydrogenation) on hydrophilic supports will operate in an aqueous environment even in a “dry” solvent like scCO₂.
- New proposed mechanism of carbonation reactions

Research Details

- Extreme scale ab initio molecular dynamics of water layer nucleation and growth at solid liquid interfaces,
- Simulation of free energy of adsorption and reactivity at a Mineral/H₂O/scCO₂ interface.

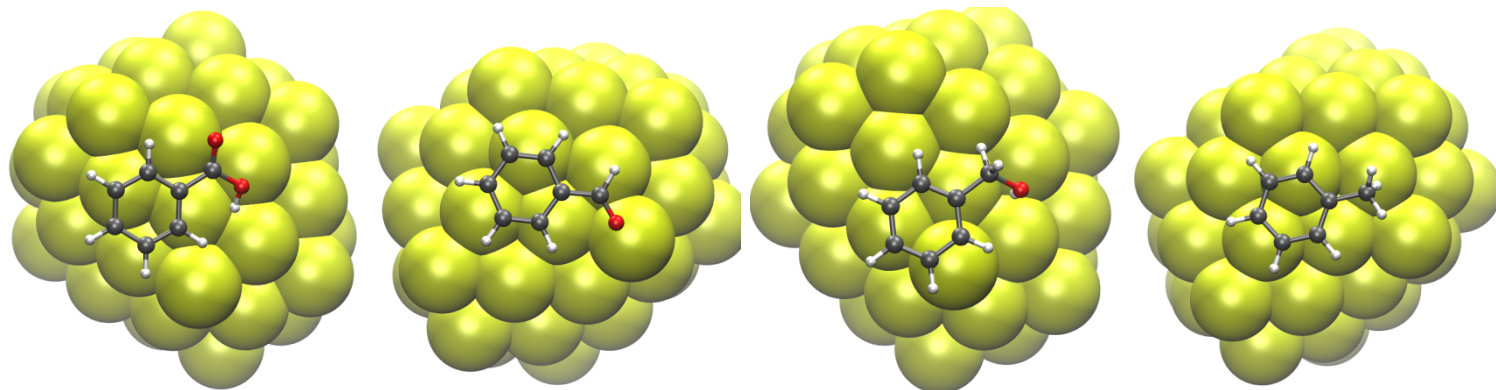
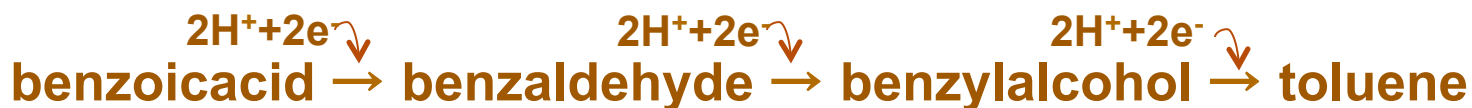


Electrochemical biomass processing.



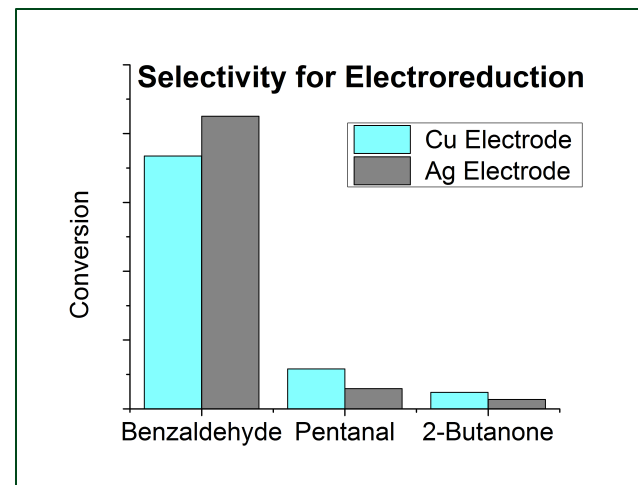
Screening of Electrocatalysts

- Nature, composition, size, of metal particle electrocatalysts
- Literature survey shows $\text{H}^+ + \text{e}^- \rightarrow 1/2\text{H}_2$ is major competing reaction w.r.t. hydrogenation.
- Screening catalysts with high H₂ overpotentials (ex Au, Cu etc.) for favorable reduction conditions for 30 reduction reactions.

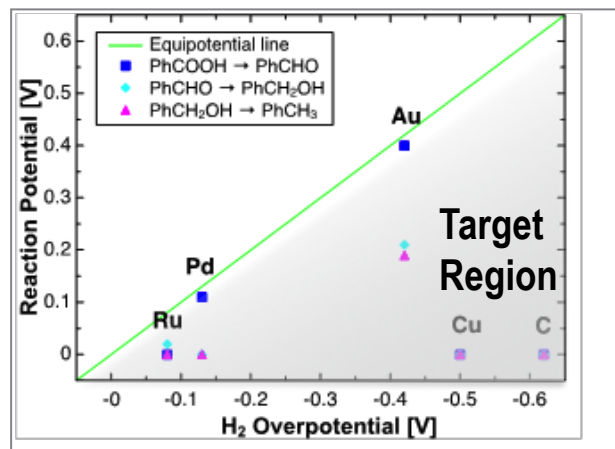


Evaluation of New Electrodes Using Theory and H-Cell Experiments

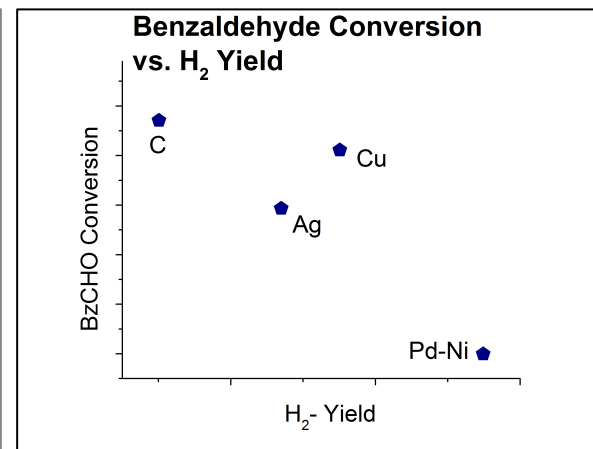
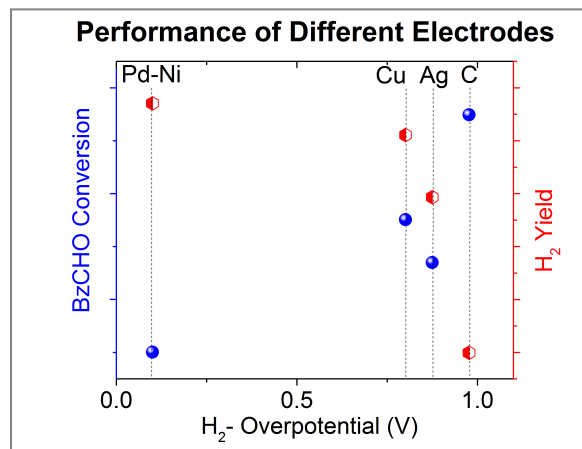
- ▶ To favor ECR over H_2 production, electrodes with higher H_2 over-potential are required
 - Theory – Cu, Au, C are favorable candidates
 - Experimental – Cu, C, and Ag could be used as new electrodes
 - Experimental – C had the lowest H_2 production and highest benzaldehyde conversion in agreement with theory
 - Theory and experiment guide new electrode development
- ▶ Aromatic aldehydes demonstrates a higher selectivity for ECR



Theoretical Prediction



Experimental Verification

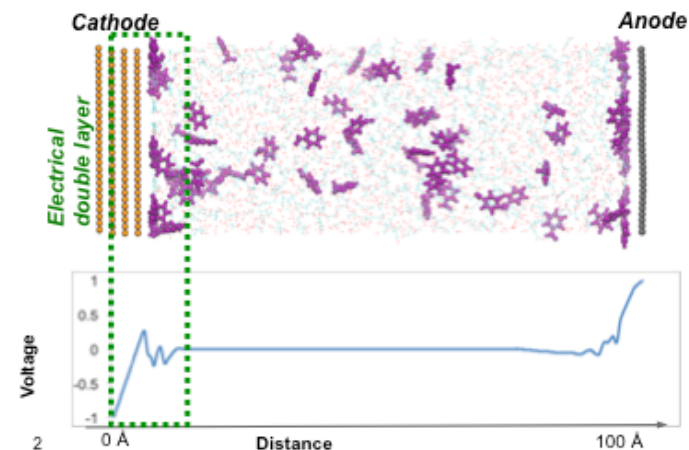


Molecular dynamics simulation of the electrode surface gives insights into selectivity and how to enhance it.

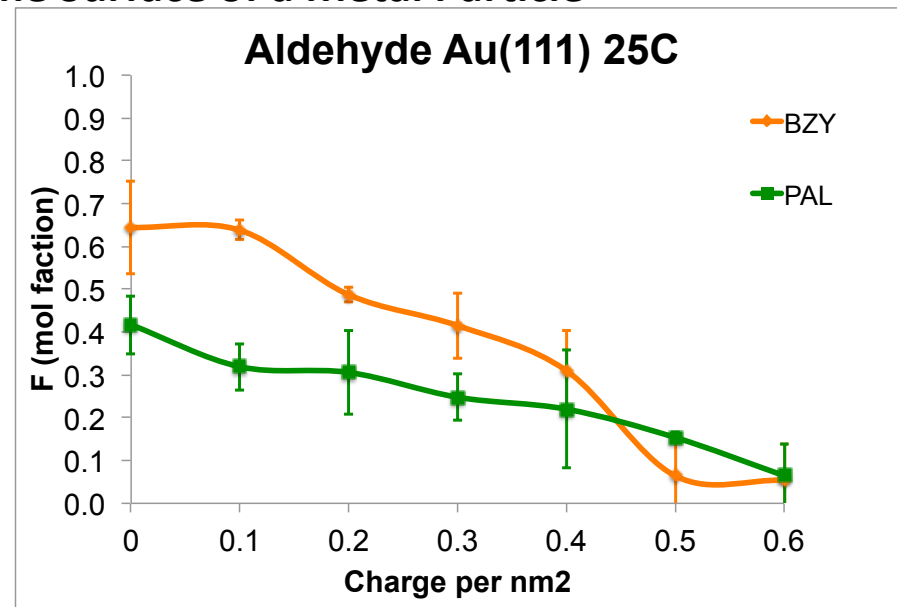
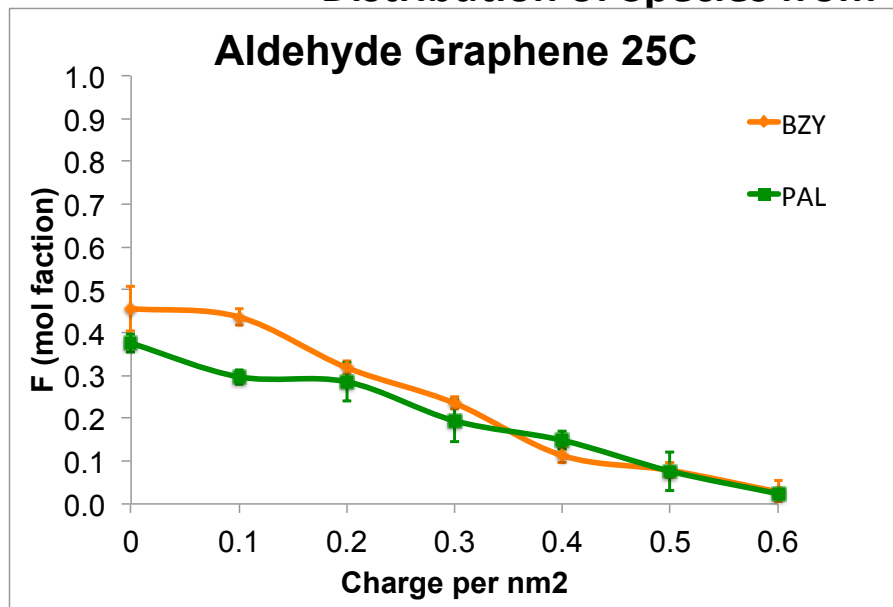
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- ▶ MD describes the environment near the electrode.
- ▶ Applied potential tends to move organics away from the metal particle.
- ▶ How can we control which species are at the surface:
 - hydrophobic/hydrophilic effects,
 - Using functionalized mesoporous carbons to control which species are near the electrodes.



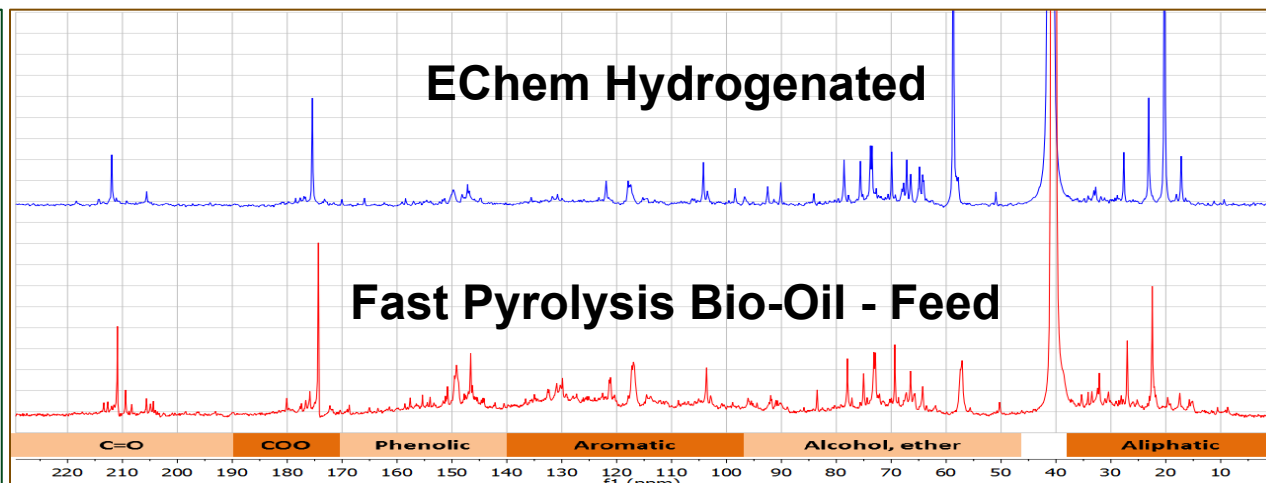
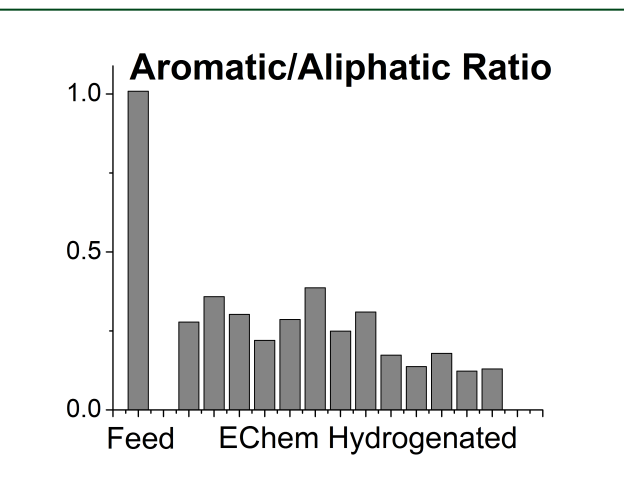
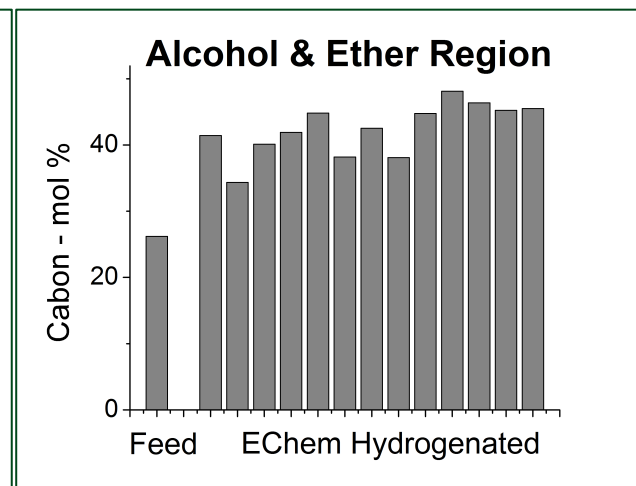
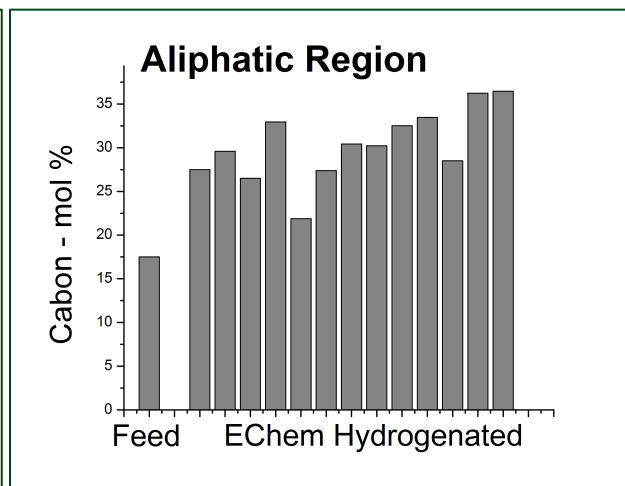
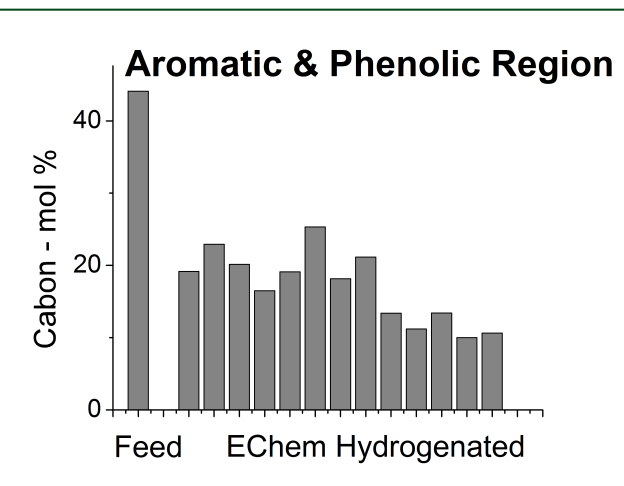
Distribution of Species from the Surface of a Metal Particle



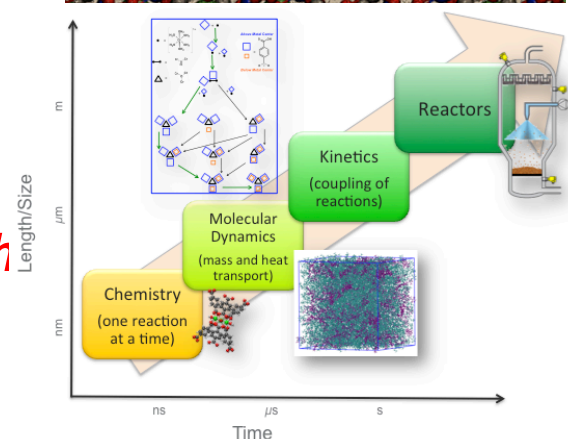
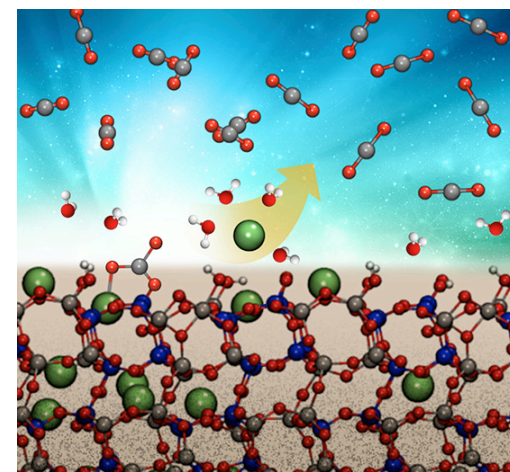
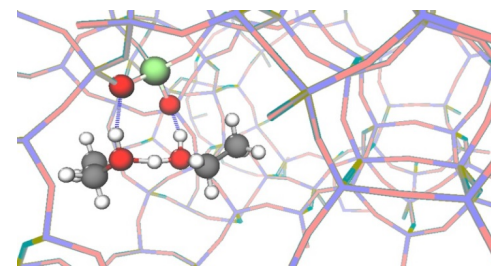


¹³C NMR Analysis of Electrochemically Hydrogenated Bio-Oil Indicated unique selectivity.

¹³C NMR suggests electrochemical hydrogenation of phenolics to aliphatic ethers



- ▶ We need to design step-change catalytic processes, enzymatic systems can inspire us: confinement, multi-functionality etc.
- ▶ We realize stable functional materials and make them (at scale) with precise control of where the active sites are in space.
- ▶ Breakthroughs in multimodal imaging and spectroscopy need to be leveraged for in-situ, ex-situ characterization.
- ▶ We need to develop a better understanding of the role of reaction environments on controlling chemical conversion (meso-scale).
- ▶ *Chemical intuition is based on enthalpy we need to build a similar intuition about entropy!*
- ▶ ***We need to integrate basic and applied research to accelerate technology development.***



Thank you!!!